

METHOD FOR REDUCING BRIGHTNESS REVERSION OF MECHANICAL
PULPS AND HIGH-YIELD CHEMICAL PULPS

Background of the Invention

5 Field of the Invention

The present invention relates to fibrous products. In particular, the present invention concerns a process for reducing the susceptibility of lignocellulosic material to unwanted brightness reversion, in particular to brightness reversion caused by light or heat.

10

Description of Related Art

It is well-known in the art that light (UV light in particular), heat, moisture and chemicals can give rise to changes in the brightness of cellulose pulps. Usually, such changes result in reduced reflectivity, particularly in blue light. This phenomenon is known as brightness reversion or yellowing and can be caused by various factors depending on which type of pulp is concerned. Heat and damp are the main causes of the brightness reversion of chemical (lignin-free) pulps, whereas mechanical pulps mostly yellow when they are exposed to light. The brightness reversion of mechanical pulps also varies depending on the raw material (type of wood), production method (with or without chemical pretreatment), and after-treatment (bleaching with different reagents) used. Thus, for instance, sulphonation and peroxide bleaching greatly increase the susceptibility of pulp to light-induced yellowing.

25 The brightness reversion of lignocellulosic pulps and products made from such pulps can be reduced or even prevented in various ways, for instance by means of impregnation or surface treatment using UV screens, antioxidants, or polymers, or by coating the surface with a coating layer or a layer of non-yellowing chemical pulp. Various additives are described in the patent literature. Thus, US 4,978,363 discloses a composition and method for treating fibers based on a mixture of an organopolysiloxane having at least one amino-substituted hydrocarbon radical directly bonded to a silicon atom and a higher fatty carboxylic acid. The carboxylic acid reacts with the amino radicals to reduce yellowing and oxidation of the fiber treatment. The composition and method provide non-yellowing

30

fibers and a treatment agent that does not gel during use, such as when exposed to carbon dioxide and/or used to treat carbon fibers.

US 6,599,326 discloses inhibition of pulp and paper yellowing using hydroxylamines and other coadditives. Chemical pulps or papers, especially kraft pulps or papers, which may still contain traces of lignin, have enhanced resistance to yellowing when they contain an effective stabilizing amount of a N,N-dialkylhydroxylamine, an ester, amide or thio substituted N,N-dialkylhydroxylamine or N,N-dibenzylhydroxylamine or an ammonium salt thereof. This performance is often further enhanced by the presence of one or more coadditives selected from the group consisting of UV absorbers, polymeric inhibitors, nitrones, fluorescent whitening agents and metal chelating agents. Combinations of hydroxylamines or their salts, benzotriazole or benzophenone UV absorbers and a metal chelating agent are, according to the cited patent, considered particularly effective. As specific examples, the patent mentions N,N-diethylhydroxylamine and N,N-dibenzylhydroxylamine.

Many of the additives that have been found to prevent yellowing are expensive or problematic from an environmental point of view; others are only effective when introduced in so large amounts that they may have a negative effect on other properties of the product or be uneconomical. Accordingly, there is still a need for methods of preventing yellowing

Summary of the Invention

It is an aim of the present invention to eliminate the problems of the prior art and to provide a new method of reducing or preventing yellowing. The method aims at effectively reducing both light- and heat-induced brightness reversion of mechanical pulps and high-yield chemical pulps.

The invention is based on the finding that the reactions that take place during oxidation, in particular enzymatic oxidation, of lignin appear to be similar to the reactions that cause brightness reversion. Therefore, the initial reaction causing brightness reversion can be activated by enzymatic or chemical means and simultaneously immediately blocked by targeted functionalization, by retarding or stopping the reactions.

Thus, the present invention provides a method of modifying fibres by bonding of new compounds to the oxidized fibres via radical pathways. In particular, the aim of the bonding of the compounds is to stabilize the structure by forming a colourless lignin derivative unable to participate in yellowing reactions.

According to the invention, new fibrous products with modified properties are produced by activating the fibres of the matrix with an oxidizing agent capable of oxidizing phenolic or similar structural groups, which may undergo reactions conducive to the formation of coloured sites on the fibres, and attaching to the oxidized sites at least one modifying agent to block the reactivity of the oxidized sites. The activation is preferably carried out enzymatically although it is equally possible to use chemical agents for achieving oxidation/radicalization.

The modifying agent has at least one functional site or reactive structure, which provides for binding of the modifying compound to the lignocellulosic fibre material, in particular at the oxidized phenolic groups or corresponding chemical structures of the fibres, which have been oxidized during the activation step.

Based on the above, the present invention provides a process for producing a fibre material having increased resistance to brightness reversion, comprising a lignocellulosic fibrous matrix with phenolic or similar structural groups and a modifying agent reducing the susceptibility of yellowing, including the steps of

- reacting the lignocellulosic fibrous matrix with an oxidizing agent in the presence of a catalyst capable of catalyzing the oxidation of phenolic or similar structural groups by said oxidizing agent to provide an oxidized fibre material, and
- contacting the oxidized fibre material with a modifying agent containing at least one first functional site, which is capable of bonding to oxidized fibre material, said modifying agent being capable of imparting to the lignocellulosic fibre material improved resistance to brightness reversion caused by light or heat or combinations thereof.

It should be noted that the term "catalyst" is to be given a broad interpretation in the present context, and it covers any agent capable of possibly – but not exclusively – in combination with a separate oxidation agent, of achieving oxidation of the phenolic or similar groups.

5

Another embodiment of the invention provides a method of reducing light or heat induced brightness reversion of mechanical or high-yield chemical pulp, comprising the steps of enzymatically or chemically oxidizing phenolic groups of the pulp and bonding to the oxidized phenolic groups a substance capable of forming a colourless lignin derivative
10 unable to participate in yellowing reactions.

More specifically, the present invention is mainly characterized by what is stated in the characterizing parts of claims 1 and 18.

15 The present invention provides important advantages. Importantly, the invention makes it possible to produce novel kinds of fibrous materials having improved brightness reversion. By means of the process, the modifying agents can be reliably attached to the fibres, and the improved resistance to yellowing will not be significantly impaired by, e.g., extensive washing of the fibres prior to forming the material into a paper or cardboard web.

20

Further details and advantages of the invention will become apparent from the following detailed description and the appended working examples.

Brief Description of the Drawings

25

Figure 1 depict in graphical form yellowing of spruce TMP samples as function of irradiation energy.

Detailed Description of the Invention

30

As mentioned above, the invention generally relates to a method of producing fibre compositions with reduced susceptibility to yellowing.

The fibre matrix comprises fibres containing phenolic or similar structural groups, which are capable of being oxidized by suitable oxidizing agents. Such fibres are typically "lignocellulosic" fibre materials, which include fibre made of annual or perennial plants or wooden raw material by, for example, mechanical, chemimechanical or chemical pulping.

5 During industrial refining of wood by, e.g., refiner mechanical pulping (RMP), pressurized refiner mechanical pulping (PRMP), thermomechanical pulping (TMP), groundwood (GW) or pressurized groundwood (PGW) or chemithermomechanical pulping (CTMP), a woody raw material, derived from different wood species as for example hardwood and softwood species, is refined into fine fibres in processes, which separate the individual

10 fibres from each other. The fibres are typically split between the lamellas along the interlamellar lignin layer, leaving a fibre surface, which is at least partly covered with lignin or lignin-compounds having a phenolic basic structure

Within the scope of the present invention, also chemical pulps are included if they are

15 susceptible to brightness reversion and have a residual content of lignin sufficient to give at least a minimum amount of phenolic groups necessary for providing binding sites for the modifying agent. Generally, the concentration of lignin in the fibre matrix should be at least 0.1 wt-%, preferably at least about 1.0 wt-%.

20 In addition to paper- and paperboard-making pulps of the above kind, also other kinds of fibres of plant origin can be treated, such as bagasse, jute, flax and hemp.

An essential feature of the invention is to block brightness reversion by modifications of phenolic hydroxyls, alfa-carbonyls and/or alfa-hydroxyls on the fibres. In particular, by

25 subjecting lignin structures to enzymatic oxidation to yield oxidized groups of the afore-said kind, the normal reactions causing brightness reversion can be attained. These reactions are then stopped by bonding a desired compound to the activated, oxidized groups.

30 In the first stage of the present process, the lignocellulosic fibre material is reacted with a substance capable of catalyzing the oxidation of phenolic or similar structural groups to provide an oxidized fibre material. Typically, the substance is an enzyme and the enzymatic reaction is carried out by contacting the lignocellulosic fibre material with an oxidizing agent, which is capable – in the presence of the enzyme – of oxidizing the

phenolic or similar structural groups to provide an oxidized fibre material. Such oxidizing agents are selected from the group of oxygen and oxygen-containing gases, such as air, and hydrogen peroxide. Oxygen can be supplied by various means, such as efficient mixing, foaming, gases enriched with oxygen or oxygen supplied by enzymatic or chemical means, such as peroxides to the solution. Peroxides can be added or produced in situ.

According to an embodiment of the invention, the oxidative enzymes capable of catalyzing oxidation of phenolic groups, are selected from, e.g. the group of phenoloxidases (E.C.1.10.3.2 benzenediol:oxygen oxidoreductase) and catalyzing the oxidation of o- and p-substituted phenolic hydroxyl and amino/amine groups in monomeric and polymeric aromatic compounds. The oxidative reaction leads to the formation of phenoxy radicals. Another groups of enzymes comprise the peroxidases and other oxidases. "Peroxidases" are enzymes, which catalyze oxidative reaction using hydrogen peroxide as their electron acceptor, whereas "oxidases" are enzymes, which catalyze oxidative reactions using molecular oxygen as their electron acceptor.

In the method of the present invention, the enzyme used may be for example laccase, tyrosinase, peroxidase or oxidase, in particular, the enzyme is selected from the group of laccases (EC 1.10.3.2), catechol oxidases (EC 1.10.3.1), tyrosinases (EC 1.14.18.1), bilirubin oxidases (EC 1.3.3.5), horseradish peroxidase (EC 1.11.1.7), manganase peroxidase (EC1.11.1.13) and lignin peroxidase (EC 1.11.1.14).

The amount of the enzyme is selected depending on the activity of the individual enzyme and the desired effect on the fibre. Advantageously, the enzyme is employed in an amount of 0.0001 to 10 mg protein/g of dry matter fiber.

Different dosages can be used, but advantageously a dosage of about 1 to 100,000 nkat/g, more advantageously 10-500 nkat/g.

In addition to enzymes, also chemical agents, such as alkali metal persulphates and hydrogen peroxide and other per-compounds, can be used for achieving oxidization of the phenolic groups and for forming phenoxy radicals. The dosage of the chemical agent is, depending on the chemical agent and on the pulp (i.e. on the amount of phenolic groups contained therein), typically in the range of about 0.01 to 100 kg/ton, preferably about 0.1

to about 50 kg/ton, e.g. about 0.5 to 20 kg/ton. In the case of chemical agents, no separate oxidation agent needs to be added. The per-compound will achieve the aimed oxidation of the phenolic groups.

- 5 The activation treatment is carried out in a liquid medium, preferably in an aqueous medium, such as in water or an aqueous solution, at a temperature in the range of 5 to 100 °C, typically about 10 to 85 °C. Normally, a temperature of 20 – 80 °C is preferred. The consistency of the pulp is, generally, 0.5 to 95 % by weight, typically about 1 to 50 % by weight, in particular about 2 to 40 % by weight. The pH of the medium is preferably
- 10 slightly acidic, in particular the pH is about 2 to 10, in the case of phenoloxidases. The chemical agents are usually employed at slightly acidic conditions, such as at pH 3 to 6. Peroxidases are typically employed at pH of about 3 to 12. The reaction mixture is stirred during oxidation. Other enzymes can be used under similar conditions, preferably at pH 2 - 10.

- 15 In the second step of the process, a modifying agent capable of reducing the susceptibility to yellowing of lignocellulosic fibres is bonded to the oxidized phenolic or similar structural groups of the matrix. Such a modifying agent typically exhibits at least one first functional site, which is compatible with the fibrous matrix, and at least one second
- 20 functional site or structure providing for the above technical effect, as will be explained in more detail below.

- The first functional site comprises in particular functional groups, which are capable of contacting and binding to the fibre at the oxidized phenolic or similar structural groups or
- 25 at its vicinity. The bond formed between the oxidized phenolic or similar residue can be covalent or ionic or even based on hydrogen bonding. Typical functionalities of the first functional site include reactive groups, such as hydroxyl (including phenolic hydroxy groups), carboxy, anhydride, aldehyde, ketone, amino, amine, amide, imine, imidine and derivatives and salts thereof, to mention some examples. Also electronegative bonds, such
- 30 as carbon-to-carbon double bonds, carbon-to-hetero atom (e.g. C=N, C=O) as well as oxo or azo -bridges can provide for bonding to the oxidized residues.

It is essential that the modifying agent is chemically or physically bonded to the fibre matrix to such an extent that at least an essential part of it cannot be removed. One

criterion, which can be applied to test this feature, is washing in aqueous medium, because often the fibrous matrix will be processed in an aqueous environment, and it is important that it retains the new and valuable properties even after such processing. Thus, preferably, at least 10 mol-%, in particular at least 20 mol-%, and preferably at least 30 mol-%, of the
5 modifying agent remains attached to the matrix after washing or leaching in an aqueous medium.

According to an embodiment of the invention, the modifying agent is activated with an oxidizing agent.

10

The interaction of the oxidized lignocellulosic material and the modifying agent, resulting in bonding of the modifying agent to the lignocellulosic material, typically takes place in liquid phase, usually in water or in another aqueous medium. The pulp or other lignocellulosic fibrous matrix is suspended in the medium and it is contacted with the
15 modifying agent or a precursor thereof, which is dissolved or dispersed in the same medium. The conditions can vary freely, although it is preferred to carry out the contacting under mixing or stirring. The temperature is generally between the melting point and the boiling point of the medium; preferably it is about 5 to 100 °C. Depending on the modifying agent or its precursor, the pH of the medium can be neutral or weakly alkaline
20 or acidic (pH typically about 2 to 12). It is preferred to avoid strongly alkaline or acidic conditions because they can cause hydrolyzation of the fibrous matrix. Normal pressure (ambient pressure) is also preferred, although it is possible to carry out the process under reduced or elevated pressure in pressure resistant equipment. Generally, the consistency of the fibrous material is about 0.5 to 95 % by weight during the contacting stage.

25

According to a particularly preferred embodiment, the first and the second stages of the process are carried out in the same reaction medium, without separating the fibrous matrix after the oxidation step. The conditions (consistency, temperature, pH, pressure) can, though, even in this embodiment be different during the various processing stages.

30

The first and the second stages of the process are carried out sequentially or simultaneously. However, it should be noted that the first step of the process aims at the formation in the fibrous substrate of phenoxy radicals, which are capable of binding modifying agents. Some modifying agents will form substrates for the oxidative enzymes

used in the invention, and in that case, it is preferred to first add the oxidative enzymes and to allow the enzyme interact with the fibrous substrate containing phenolic or similar groups, e.g. for 0.1 to 180 minutes, in particular about 1 to 30 minutes to achieve oxidation of the phenolic groups, and to add the modifying agents after the enzymatic oxidation.

5

The same observations are true for the chemical oxidation agents mentioned above. As Example 3 shows, reasonably good results are obtained with the simultaneous application of oxidation agent and modifying agent, although the best results are attained when steps one and two are carried out sequentially.

10

According to one preferred embodiment, the modifying agent is an aliphatic or aromatic, monocyclic, bicyclic or tricyclic substance. The aliphatic compound can be an unsaturated carboxylic acid, advantageously a monocarboxylic unsaturated fatty acid, having 4 to 30 carbon atoms. In particular, the modifying agent can be a monocarboxylic, unsaturated fatty acids containing a minimum of two double bonds, preferably two conjugated double bonds. Such fatty acids have an even number of carbon atoms, typically in the range of 16 to 22. It is also possible to use lower alkanols, i.e. alcoholic compounds comprising 1 to 6, in particular 1 to 4 carbon atoms. Examples include n- and i-propanol and n- and t-butanol.

15

Examples of particularly suitable compounds are constituted by linoleic and linolenic acid. It would appear that the unsaturated fatty acid bonds to the oxidized groups or structure via one of the double bonds.

20

Other suitable compounds include antioxidants, such as tocopherol and beta-carotene.

25

The compound can have special properties, such as capability to trap radicals and form colourless substituents.

30

The above two steps can be carried sequentially or simultaneously. Also other compounds, such as papermaking chemicals may be present during the reaction steps.

After the above processing, the modified fibre having new properties is generally separated from the liquid reaction and further used in target applications.

The following non-limiting examples illustrate the invention:

Example 1

5 A 5 g portion of bleached spruce TMP was suspended in water. The pH of the suspension was adjusted to pH 4.5 by addition of acid. The suspension was stirred at RT. Laccase dosage was 1000 nkat/g of pulp dry matter and the final pulp consistency was 7.5 %. After 30 minutes laccase reaction, 0.15 mmol linoleic acid/g of pulp dry matter was added to the pulp suspension. After 1 h total reaction time, the pulp suspension was filtered and the pulp
10 was washed thoroughly with water. Handsheets were prepared. For comparison purposes, reference treatments were carried out using the same procedure as described above but without addition of laccase or linoleic acid or both. The light-fastness on the pulps was tested with Xenotest 150S light exposure and weathering test instrument using "window glass" filter. The brightness of the handsheets was measured as function of irradiation
15 dosage. The results are presented graphically in Fig. 1.

From the results presented in Fig. 1, it is apparent that the addition of linoleic acid and laccase was found to decrease the yellowing tendency of the pulp. In other words, addition of a modifying agent in the presence of an oxidizing agent and a suitable catalyst, the
20 yellowing tendency of pulp was decreased.

Example 2

Bonding of new compounds to TMP

25 A 5 g portion of spruce TMP was suspended in water. The pH of the suspension was adjusted to pH 4.5 by addition of acid. The suspension was stirred at RT. Laccase dosage was 1000 nkat/g of pulp dry matter and the final pulp consistency was 7.5 %. After 30 minutes laccase reaction the new compound was added to the pulp suspension. After 1 h total reaction time, the pulp suspension was filtered and the pulp was washed thoroughly
30 with water. Handsheets were prepared. For comparison purposes, reference treatments were carried out using the same procedure as described above but without addition of laccase or the new compound. The light-fastness on the pulps was tested with Xenotest 150S light exposure and weathering test instrument using "window glass" filter. The changes in the ISO brightnesses after irradiation are summarized in Table 1.

Table 1

Treatment	Irradiation (Whm²)	Δ Brightness (as ISO- Brightness)
TMP Reference	1260	10
TMP + laccase + ferulic acid (0.15 mmol/g)	1260	3
TMP + laccase + vinyl laurate (0.3 mmol/g)	1260	2

5 Example 3

Sample A: Peroxide bleached aspen-CTMP-pulp was treated with sodium persulphate (dosage 5 kg/ton of pulp) and linoleic acid (5 kg) at 80 °C, at pH 5 for 60 minutes. The treatment was carried out at a consistency of 10 %.

10

Sample B: The pulp sample was treated in the same way as Sample A except that ammonium persulphate (5 kg) was used instead of Na-persulphate.

Sample C: The pulp sample was treated in the same way as Samples A and B except that
15 hydrogen peroxide was used instead of persulphate. The pH of the test was 4.

Sample D: The pulp sample was treated as Sample A but t-butanol (5 kg) was used instead of linoleic acid.

20 Sample E: The pulp sample was treated in the same way as Sample A, but no linoleic was added. After the treatment with persulphate, a separate treatment was made with linoleic acid (5 kg) at 80 °C at a consistency of 10 %. The duration of the treatment was 30 min, and the pH was 5

25 Sample F: The sample was prepared as Sample D, but without using any t-butanol. After the persulphate treatment, a separate treatment (30 min, pH 5) with t-butanol was carried out at a consistency of 10 % and a temperature of 80 °C, the dosage being 5 kg/ton of pulp.

Sheets were manufactured from the pulp samples and their brightness stability was tested with a Xenotest S150 using a "window pane" filter. The radiation of the Xenotest – apparatus corresponded to that of sunlight through a window pane, but the intensity of the radiation was much stronger (accelerated test). The brightness of the samples was
5 determined after a 2 h radiation (corresponds to 1260 wh/m²)

The results are indicated in Table 2 below:

10	Table 2	
	Sample	Brightness reduction (Δ Brightness, %ISO)
	Reference (untreated)	10.4
	A	6.9
	B	7.2
15	C	6.8
	D	7.2
	E	6.1
	F	6.1

20

As apparent from the above results, the brightness stability of the samples treated by the present invention has been improved by even more than 4 units.

25